REVISTA MATÉRIA V.27 N.01

ISSN 1517-7076 artigos e13164, 2022

Characterization and Evaluation of Syenite rocks of Poços de Caldas (MG - Brazil) in the Manufacture of Frit and Glazes

José Tadeu Gouvêa Junior[1], Sylma Carvalho Maestrelli[1], Luciano Luis da Silva[2], Carolina Del Roveri[1]

[1]Universidade Federal de Alfenas, Campus Poços de Caldas, Instituto de Ciência e Tecnologia, Rod. José Aurélio Vilela, BR 267, Km 533, 11999, Cidade Universitária, CEP: 37715-400, Poços de Caldas, MG, Brasil
[2]Thermoceram Ltda, Av. Eng. Ronaldo Algodoal Guedes Pereira, 391 - Parque Industrial Mogi Guacu, CEP: 13849-210, Mogi Guaçu, SP, Brasil
e-mail: ze.engminas@gmail.com, sylma.maestrelli@unifal-mg.edu.br, carolina.roveri@unifal-mg.edu.br, master.lucianosilva@gmail.com

ABSTRACT

The present work aimed to characterize the firing behavior of glazes formulated using samples of rocks from the region of Poços de Caldas as a substitute for feldspar. Four formulations were performed, using samples before and after a magnetic separation process. The raw materials were analyzed for their chemical-mineralogical characteristics and the formulations were characterized using Binil Surface Application and fusibility button test, in colorimetric and brightness analyzes. The formulations were also characterized for their coloration compared to the standard glaze, holding nepheline. It was verified that the potassium rock sample presented dark colors (post-magnetic separation), making it impossible to use. The foyaite samples showed promising results, before and after the magnetic separation. According to the results of the colorimetric analysis as the fusibility tests were performed, the non-magnetic samples were clearer due to a comparison of the standard sample of nepheline in both fluorescent light and sunlight, indicating that these samples have potential for use in the formulation of glazes and are interesting alternatives to nepheline and feldspars.

Keywords: foyaite, syenitic rocks, glazes, flux

1. INTRODUCTION

In Brazil, the main consumers of feldspar ((K, Na, Ca) (Si, Al)$_4$O$_8$) as raw material are the ceramic and glass industries. The feldspar can act as a fluxing agent (decreasing melting temperature), as well as a supplier of silica (SiO_2), alumina (Al_2O_3) and alkaline oxides (Na_2O and K_2O), which are applied to increase the hardness and chemical resistance, replacing the use of sodium carbonate (Na_2CO_3) on these industries [1-3].

Feldspars can also be used on plastics, rubbers, light abrasives and as mineral fillers for paint industries.

In some applications, the feldspars may be replaced by agalmatolite, feldspathic sand, clay, blast furnace slag, phyllite, nepheline syenite, pyrophyllite and talc [1-4].

Its production in 2013 was of 320,048 t, with the state of Paraná handling 54.8% of the gross production, while other states presented the following percentages: Santa Catarina (15.7%), Paraíba (11.5%), Rio Grande do Norte (6.2%), Minas Gerais (6.1%), Bahia (5.0%), São Paulo (0.5%) and Pernambuco (0.2%).

The processing production generated an amount of 294,357 t, distributed as follows: Paraná (60.6%), Minas Gerais (34.3%), Rio Grande do Norte (4.3%), São Paulo (0.5%), and Paraíba (0.3%) [3].

The Financial Compensation of Mineral Resources (CFEM) for feldspar on 2013 was R$ 1,016 million compared to R$ 85,000 in 2005, i. e., there was a 1,095% increase over eight years [3].

The finishing of most industrial ceramics is achieved by applying and then firing a ceramic composition called glaze, which is more fusible than the support.

The glaze is a thin vitreous layer (typically around 0.15 mm to 0.5 mm thick) formed on the ceramic body.

Autor Responsável: José Tadeu Gouvêa Junior Data de envio: 04/04/2019 Data de aceite: 29/07/2020

10.1590/S1517-707620220001.1364

A suspension of some raw materials is applied on the ceramic body and then firing is performed at a temperature suitable for this mixture to flow with a certain proper viscosity on the surface of the support and for the compounds to have a good dissolution in order to ensure their coating [5].

The support is a ceramic body that sinters during the firing and develops a glassy phase with wide dimensional variations and a broad sense, in the order of 15%. [12]

The glaze produces a significant amount of glass phase during firing to the extent that all the raw materials in the glaze become viscous liquids that flow through the inclined surfaces, filling in the surface gaps and producing, during cooling, a glaze having important surface properties, such as [6, 7]:

- Technological - water and gases impermeability, greater mechanical resistance for the support, resistance to scratches and to chemical inertia;
- Aesthetic and decorative - texture, finishing and shine;
- Functional - easy cleaning;

Glazes are indispensable on some sintered ceramics such as stoneware and porcelain, because, besides eliminating some imperfections on the surface, they also influence the mechanical resistance of the body.

The use of feldspar for formulation in ceramic industries should be ideal; however, the production of this mineral is low, and its extraction and processing are too expensive. Therefore, industries, especially the ones dealing with vitreous materials, must resort to other sources for the manufacture of ceramic materials; sometimes nepheline ($NaAlSiO_4$) is used because it has physicochemical structures similar to feldspars and a lower price [8-9].

Therefore, due to the growing demand for feldspar in the ceramic industry, its increasing import rate and the high prices for processing it, there is a need to find alternative sources for the formulation of ceramic pieces at lower costs with characteristics similar or superior to those already produced [10].

The use of this mineral for the glass industry is conditioned by the iron and titanium contents present on the extracted samples, with the iron content not exceeding 0.1 wt % as Fe_2O_3, except in manufacture glasses with darker colors such as amber. On the other hand, the ceramic industries follow the same margin of tolerance for the formulation of materials considered as white ceramics. Thus, it is necessary to remove these components using expensive processes such as magnetic separation or flotation [11].

A workable alternative to meet the demand are the syenitic rocks bearing nepheline (Na, K) ($AlSiO_4$). After ore processing in order to reduce its iron content, these rocks can be used for the formulation of frits and glazes, reducing the need to import feldspar, creating new opportunities for ceramic industries and increasing profits at cities where there are large concentrations of this mineral, such as Poços de Caldas - MG [4, 12-14].

The aim of this work is to analyze an alternative to feldspar, i.e., the concentration of the nepheline phase (which must have an iron content below 1 wt %) and its applications in the formulation of frits and glazes as compared to the standard formulation.

2. MATERIALS AND METHODS

The processing of nepheline rock is primordial for iron excess removal. According to the literature, the Fe_2O_3 should not exceed 0.1wt %. The method followed these steps:

Firstly, the raw materials were characterized, then samples were processed and characterized again after the processing, and finally frits and glazes were formulated with the raw materials before and after the processing.

The characterization of samples was made from chemical and mineralogical points of view and went through the magnetic separation process of potassium rock of the Massif comminuting below 325 mesh (45 μm). For study purposes, one sample was appointed as 'potassium rock' and the other as 'foyaite', according to the nomenclature used by the Curimbaba Mining exploration team, unrelated to the Petrographic classification.

With the post-processing products, it was possible to formulate glazes and frits from a standard formulation and nepheline standard. Thus, it was possible to compare the standard glaze sample with the rock samples, where the nepheline was replaced by the rock samples before and after processing, which are described in Table 1, CMC being the carboxymethylcellulose used as a binder and HMF the sodium hexametaphosphate used as deflocculant.

Table 1: Description of the glazes of different compositions

Standard formula	Amount (%)				
Formulations	F1	F2	F3	F4	F5
FRIT MATTE	57.50	57.50	57.50	57.50	57.50
KAOLIN	5.00	5.00	5.00	5.00	5.00
NEPHELINE	35.00	35.00*	35.00**	35.00***	35.00****
ALUMINA	2.00	2.00	2.00	2.00	2.00
CMC	0.30	0.30	0.30	0.30	0.30
HMF	0.20	0.20	0.20	0.20	0.20

* magnetic foyaite; ** non-magnetic foyaite; *** non-magnetic potassium rock; **** magnetic potassium rock

2.1. Characterization of the raw material

The characterization of the raw materials was performed with chemical analysis techniques by X-Ray Fluorescence on samples before and after ore processing. For the chemical composition of the samples, the X-Ray Fluorescence Philips 1000 equipment was used, adopting the pressing and semi-quantitative screening methods. The mineralogical analysis was performed by X-Ray Diffraction, in the same conditions as the chemical analysis. An X-Ray Diffractometer PanAnalytical was used. The measures were made with Cobalt radiation (wavelength = 1.7893 Å). The goniometer speed had pass equal 0.05 grades and exposition time of 0.8 sec/pass. The data evaluation was performed in the High XPERT Plus software.

2.2. Magnetic separation

The magnetic separation experiments of the potassium rock and the foyaite patterns were carried out wet in a WHIMS (Wet High Intensity Magnetic Separator) with INBRAS matrix separation of steel screen, with the magnetic field intensity able to reach 13,000 Gauss.

The magnetic separation tests occurred with varied amperage, in which the suspension passed through the magnetic matrix. The amps used were 0, 5, 10, 15 and 20 A. The magnetic and non-magnetic products obtained were weighed and dried, and then used to formulate the glazes and frits to compare the visual effects of the separation.

2.3. Glazes and fusible buttons for superficial observation

For the formulation of the glazes and fusibility buttons, different compositions were tested based on the standard nepheline, where the nepheline of the base sample was replaced by non-magnetic foyaite, foyaite, potassium rock and a non-magnetic potassium rock, as showed in Table 1.

The procedure for the formulation of these compounds was developed by the group with the consultancies of a supplier of inputs for the ceramic industry, following these steps: the starting reagents were weighed using the semi-micro analytical balance Digimed model DG - 5000, with a base of 100 g, milling in the porcelain rapid mill jar, Servitech MA360 / P - planetary mill model, with ¼ of its volume filled with alumina grinding bodies, for 40 min with 40% of water, where the residue passed through a sieve of 325 mesh. Then, a part of this compound was packed in a stainless-steel container and dried in an oven (model SL 102/221 of SOLAB) at 110 ºC for 48 h, and the other part was packed in 1 L amber bottles for later application on non-glazed ceramic surface through the Binil application.

After oven drying, the dried samples were ground and homogenized in agate mortar for 20 min and passed through a 200-mesh sieve. After sieving, 10% of water was conditioned to its pass-through volume to homogenize the samples to be pressed. After the homogenization of the samples, they passed twice through a 24-mesh sieve in order to homogenize its volume of water. The samples were then packed in polymer containers and kept closed to prevent loss of moisture.

After 24 h the samples were duly weighed to keep the same thickness of material for all the samples and pressed to 243 kgf/cm^2 in a Marcon Uniaxial Press with capacity of 10 ton to be burned later in a muffle EDG 3000 with different temperatures and with baseline of 5 min.

The different compositions tested underwent the same procedure for their production, replacing the nepheline of the standard formula with non-magnetic foyaite, magnetic foyaite and a non-magnetic potassium rock. The results are presented below.

2.4. Colorimetry and Brightness Measure

The colorimetric coordinates were acquired using the CIElab (Commission International de I'Eclairage) method, which measures the intensity of the variation in the direction of the parameters of the system and

characterizes the color of the samples obtained under various sources of light and illuminants to avoid metamerisms. The colorimetric analysis using CIElab standards can be used to compare the parameters composed of three axes L *, b * and a *, where: L * (brightness ranging from 0 (black) to 100 (white)), b * (+ b yellow and -b blue) a * (+ a red and -a green). The reflectance in the region of the visible and the colorimetric of the materials were typed using the Color Touch colorimeter, under the action of source D65 at an angle of 10º and some illuminants (D65, F7). The term light source refers to the actual light reaching a sample, while the illuminants are the result of a spectral distribution that simulates the ordinary operating conditions on a day-to-day basis. In this work we used sunlight and fluorescent light (cold light). The transparency of frits was measured with a spectrophotometer (Minolta CR 400). The results were expressed in the chromatic coordinates L *, a * and b *. The brightness of the frits (β) was determined using a brightness meter (Ericksen Picogloss 500 MC).

3. RESULTS AND DISCUSSION

3.1 X-Ray Fluorescence and X-Ray Diffraction – Raw materials before processing

The X-ray fluorescence chemical analyzes, presented on Table 2, were performed to obtain the concentrations of elements present in the formulation's raw materials, and it is important to note that the aim of the production of frits and glazes is that the average of iron content be below 1wt% [5]. The flux raw materials have high iron content (class 0-1), according to DONDI [15] and, consequently, extremely high fusibility.

Table 2: Chemical Analysis – Dry Base of raw materials of formulation. Observe the values for non-processing raw samples. * L.O.I. = Loss on ignition

Component (%)	Raw Materials					
	Frit Matte	Kaolin	Nepheline	Foyaite	Potassium Rock	Alumina
L.O.I.*	0.20	13.70	1.8	4.95	1.74	0.00
SiO_2	52.90	46.68	58.7	52.8	59.2	0.00
TiO_2	0.00	0.00	1.25	0.78	1.28	0.00
Fe_2O_3	0.0	0.32	4.92	2.59	4.95	0.06
K_2O	3.17	0.64	13.9	11.1	13.4	0.00
Al_2O_3	15.34	38.44	18.1	26.9	18.2	99.42
CaO	15.04	0.03	0.02	0.03	0.04	0.00
P_2O_5	0.00	0.13	0.11	0.13	0.11	0.00
MnO_2	0.00	0.00	0.05	0.15	0.05	0.00
ZrO_2	0.00	0.00	0.24	0.11	0.25	0.00
MgO	2.21	0.00	0.01	0.13	0.04	0.00
Na_2O	0.84	0.02	0.64	0.05	0.65	0.02
Cr_2O_3	0.00	0.00	0.01	0.01	0.01	0.00
BaO	4.52	0.00	0.00	0.00	0.00	0.00
ZnO	5.84	0.00	0.00	0.00	0.00	0.00

The supplier of alkalis raw materials presents high concentrations of SiO_2, which is widely used as a flux for ceramic production, and high concentrations of Al_2O_3, used to increase the durability of materials.

The analyzes for loss on ignition, which is about 1.74% for the sample of potassium rock and 4.95% for the sample of foyaite, may show the presence of carbonates or organic matters present in the material which can cause increases in the concentration of the oxides after the firing process.

The mineralogical analysis is presented in Table 3.

Table 3: Mineralogical Analysis of raw materials.

Mineralogical Phases	Kaolin	Nepheline	Foyaite	Potassium Rock	Alumina
Quartz	x				
Hematite			x	x	
Goethite			x	x	
Magnetite			x	x	
Nepheline		x	x	x	
Leucite		x	x		
Microcline and other K-feldspar	x	x	x	x	
Gibbsite	x	x	x	x	x
Muscovite	x	x	x	x	
α-Alumina					x

It was possible to identify these oxides in their mineral phases in the mineralogical analysis on the potassium rock sample, where the main phases were $KAlSi_3O_8$ - microcline, $Al(OH)_3$ - Gibbsite and Fe^{+} $2Fe_2^{+}$ $3O_4^{-}$ Magnetite, while in the foyaite sample there are the same mineral phases as the potassium rock and Leucite.

3.2. Magnetic separation

The objective of the magnetic separation operation was to reduce the Fe_2O_3 or/and Fe_3O_4 content of the samples, which was 4.95 wt % in the sample of potassium rock and 2.59 wt % in the sample of foyaite, to less than 1 wt %, which is the appropriate content when applying in glazes and frits. The samples were suspended and passed through a magnetic separator of the WHIMS type with different currents, and the magnetic and non-magnetic samples were dried for further analysis by fluorescence, which will be presented next. Table 4 shows the distribution of masses retained at each current intensity applied in the magnetic separation test, while Table 5 presents the results for the mass recovery of the samples after the magnetic separation tests.

Table 4: Results of magnetic separation

	Magnetic Separation - WHIMS for the Potassium Rock sample		Magnetic Separation – WHIMS for the foyaite sample	
Sample – Current (A)	Mass (g)	Mass (%)	Mass (g)	Mass (%)
Magnetic – 0	1.00	0.06	54.90	1.21
Magnetic – 05	9.50	0.57	550.20	12.11
Magnetic – 10	7.90	0.47	369.80	8.14
Magnetic – 15	7.90	0.47	84.30	1.86
Magnetic – 20	14.50	0.86	33.50	0.74
Non-magnetic	1,640.40	97.57	3,450.00	75.95
Total calculated	1,681.20	100.00	4,542.70	100.00
Total analyzed	1,765.00	100.00	5,000.00	100.00
Losses	83.80	4.75	457.30	9.15

Table 5: Results of mass recovery

	Mass Recovery of potassium rock (%)	Mass Recover of foyaite (%)
Concentrate (Nonmagnetic)	92.94	69.00
Reject (Magnetic)	2.41	21.85

Figure 1 shows the distribution of the obtained data in relation to the accumulated retained mass content (%) and the current intensity for the magnetic separation of the potassium rock and the foyaite, respectively.

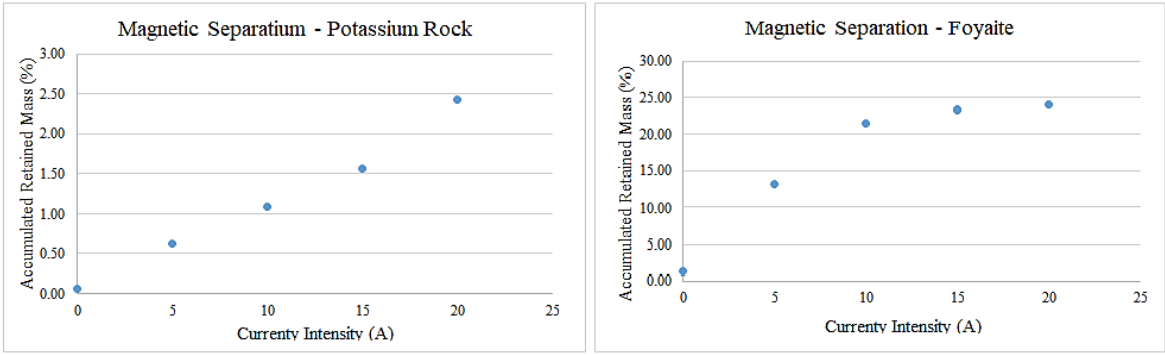

Figure 1: Magnetic separation of potassium rock and foyaite

It is possible to see that as the intensity of the current and magnetic field of the equipment increases, a larger retained mass is obtained, that is, the larger the applied field, the greater the efficiency of the separation. It can be noticed that the mass recovery of the sample of potassium rock, as compared to the sample of foyaite, was much higher; however, the concentration of magnetic reject in the samples had an inverse relation. That difference of concentrations can indicate that the sample of foyaite presented better results to the magnetic separation tests than the samples of potassium rock, and the analysis of the results of the X-Ray Fluorescence after processing will confirm if the magnetic separation was efficient.

3.3. X-Ray Fluorescence and X-Ray Diffraction – Raw materials after processing

The post-processing X-ray fluorescence chemical analyzes presented in Table 6 were performed to obtain the concentrations of elements present in the samples after the processing step to verify if the iron content present in the samples had decreased and if it was below 1%.

Table 6: Chemical analysis (wt%) of syenitic rocks after processing. * L.O.I. = Loss on ignition

Material: Potassium Rock – Non-Magnetic		Material: Foyaite – Non-Magnetic	
L.O.I.*	1.59	L.O.I.*	3.37
SiO_2	59.80	SiO_2	59.90
TiO_2	1.25	TiO_2	0.55
Fe_2O_3	3.79	Fe_2O_3	0.89
K_2O	13.90	K_2O	10.70
Al_2O_3	18.40	Al_2O_3	19.50
CaO	0.04	CaO	1.18
P_2O_5	0.10	P_2O_5	0.09
MnO_2	0.04	MnO_2	0.03
ZrO_2	0.24	ZrO_2	0.08
MgO	0.04	MgO	0.04
Na_2O	0.67	Na_2O	3.51
Cr_2O_3	0.01	Cr_2O_3	0.00

From the chemical analysis of the post-processing raw materials it can be verified that the content of iron-containing phases decreased significantly for the sample of foyaite, reducing the content of iron oxide from 2.59 wt% to 0.89 wt%%. The sample of potassium rock, on the other hand, presented values above 1 wt% of iron oxide, despite a remarkable reduction in the content of 4.92 wt% to 3.79 wt%% post processing, meaning that these samples did not achieve the value for its use as frit or glazes.

3.4. Glazes and fusible buttons

Five different compositions were made for the formulation of the glazes and the fusibility buttons: F1, F2, F3, F4 and F5, as shown in Table 1. The same proportions used in the standard F1 formulation were used for the formulation of the other samples, except that the nepheline of the standard sample was replaced by the samples of foyaite before (also called 'total sample') and after the processing and the sample of potassium rock before (also called 'total sample') and after processing. All the raw materials were below 200 mesh (74 μm).

After the procedures for the preparation of the glazes and buttons showed in Figure 1, they were applied to ceramic bodies with two test bases: a clear base which would simulate the light ceramic base and a dark base representing the reddish or brown ceramic base with the aid of a Binil applicator and

brought to the melt at 1150 °C in order to verify the formation of glaze on these bodies and compare them with the standard sample, as can be seen in Figures 2 and 3.

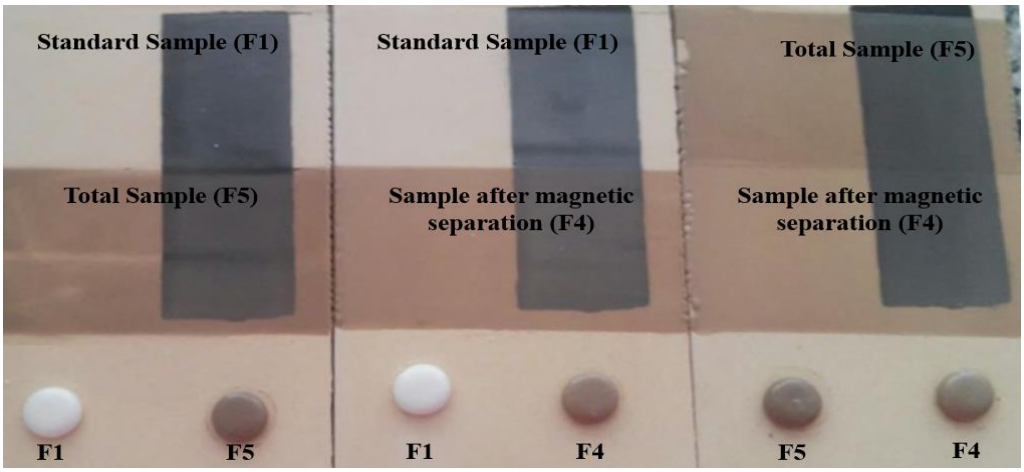

Figure 2: Binil surface application for the formulations of potassium rock before (F5) and after processing (F4) along with their pressed buttons and comparisons with the standard samples of nepheline (F1).

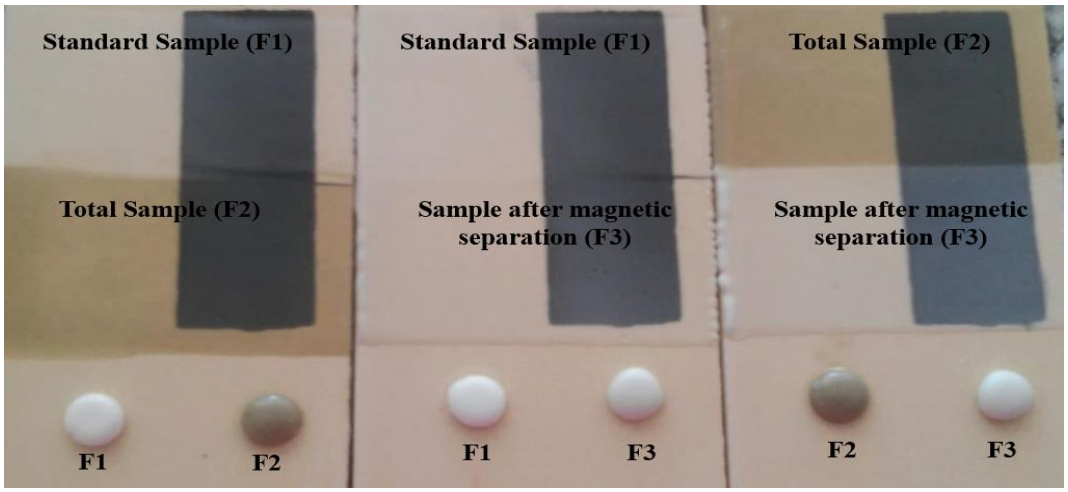

Figure 3: Binil surface application for the formulations of foyaite before (F2) and after processing (F3) along with their pressed buttons and comparisons with the standard samples of nepheline (F1).

In Binil surface application, the test specimens presented interesting superficial characteristics and can be commercially practical according to the type of support, as seen in Table 7.

Table 7: Superficial characteristics of buttons and Binil surface application.

	F1	F2	F3	F4	F5
Glazing			Yes		
Color	White	Grey	White grey	Light brown	Deep brown
Brightness			Yes		
Glaze arrangement - support	Suitable	Suitable	Suitable	Inappropriate	Inappropriate

3.5. Colorimetry

After the firing test carried out at 1150 °C, which was promising, new tests were carried out with larger press bodies in order to verify the difference in fusibility and formation of vitreous-like materials as the ones obtained in samples at higher temperatures (1060 °C, 1080 °C, 1100 °C, 1120 °C, 1140 °C, 1180 °C and 1200 °C). Also, the colorimetric appearance of the samples was checked, as can be observed in Tables 8 and 9, showing the solar and fluorescent reference, respectively:

Table 8: L*, b* and a* values and brightness (β) for samples of fusible buttons at different temperatures with reference to sunlight (6500 K).

Material	**Nepheline (F1)**				**Magnetic Foyaite (F2)**				**Non-magnetic Foyaite (F3)**			
Temperature	L*	a*	b*	β	L*	a*	b*	β	L*	a*	b*	β
1060 °C	96.48	+0.58	+3.33	8.6	74.17	+10.16	+9.70	7.4	92.42	+1.98	+7.32	7.8
1080 °C	96.86	+0.38	+2.71	9.2	77.24	+7.50	+12.01	7.6	93.81	+1.22	+6.50	8.2
1100 °C	96.78	+0.37	+2.72	9.4	74.9	+7.90	+14.48	7.6	93.65	+1.01	+6.11	8.5
1120 °C	96.84	+0.37	+2.69	9.8	75.26	+7.76	+14.73	7.7	93.87	+0.99	+6.01	9.0
1140 °C	91.86	+0.30	+4.14	10.1	67.82	+4.62	+22.41	8.1	87.64	+0.84	+7.06	9.2
1180 °C	91.50	+0.28	+4.25	10.2	67.5	+4.52	+22.95	8.1	87.42	+0.82	+7.26	9.7
1200 °C	91.42	+0.26	+4.44	10.3	67.35	+4.50	+23.11	8.6	87.36	+0.73	+7.35	9.9

Non-magnetic Potassium Rock (F4)				**Potassium Rock Magnetic (F5)**			
L*	a*	b*	β60	L*	a*	b*	β60
85.47	+1.20	+8.93	7.4	65.22	+9.40	+11.25	6.8
82.28	+3.42	+14.47	7.6	68.44	+9.27	+17.80	7.2
80.73	+3.71	+16.02	8.3	65.42	+9.52	+19.44	7.4
78.83	+4.03	+17.19	9.1	58.99	+10.15	+21.22	7.7
70.53	+3.98	+20.94	9.2	57.25	+10.26	+23.15	8.5
70.24	+3.80	+21.24	9.4	54.18	+10.56	+23.99	8.7
69.95	+3.76	+21.55	9.9	49.47	+10.74	+23.74	8.9

Table 9: L*, b* and a* values and brightness (β) for samples of fusible buttons at different temperatures with reference to fluorescent light (cold light – 4230 K).

Material	**Nepheline (F1)**				**Magnetic Foyaite (F2)**				**Non-magnetic Foyaite (F3)**			
Temperature	L*	a*	b*	β	L*	a*	b*	β	L*	a*	b*	β
1060 °C	96.70	+0.34	+3.82	8.4	75.05	+7.58	+11.37	7.1	92.95	+1.23	+8.47	7.4
1080 °C	97.03	+0.21	+3.06	8.8	78.15	+5.37	+13.81	7.2	94.24	+0.71	+7.41	7.6
1100 °C	96.95	+0.21	+3.07	9.2	75.95	+5.58	+16.58	7.4	94.04	+0.59	+6.94	7.6
1120 °C	97.01	+0.21	+3.04	9.3	76.33	+5.44	+16.87	7.5	94.26	+0.58	+6.83	8.2
1140 °C	92.05	+0.19	+4.59	9.8	69.21	+2.87	+25.21	7.9	88.03	+0.52	+7.89	8.3
1180 °C	91.88	+0.15	+5.36	10.1	68.69	+2.50	+25.96	7.9	87.55	+0.49	+8.13	8.3
1200 °C	91.42	+0.12	+5.45	10.1	68.52	+2.24	+26.11	7.9	87.21	+0.47	+8.42	8.5

Non-magnetic Potassium Rock (F4)				**Potassium Rock Magnetic (F5)**			
L*	a*	b*	β60	L*	a*	b*	β60
86.05	+0.75	+10.24	7.2	65.22	+9.40	+11.25	6.4
83.25	+2.05	+16.44	7.4	68.44	+9.27	+17.80	6.8
81.79	+2.24	+18.16	7.6	65.42	+9.52	+19.44	7.1
79.96	+2.44	+19.46	8.3	58.99	+10.15	+21.22	7.4
71.81	+2.40	+23.46	8.5	57.25	+10.26	+23.15	7.6
70.54	+2.39	+24.22	8.8	54.18	+10.56	+23.99	7.8
70.22	+2.36	+25.39	9.0	49.47	+10.74	+23.74	8.4

The colorimetric analyzes indicated that, as the fusibility tests were performed, the samples of non-magnetic foyaite got closer due to the comparison of the L * parameters, equating to the standard sample of nepheline in both fluorescent light and sunlight, since these samples have ratios of yellow and red b * and a * slightly larger than the standard samples, while the samples of magnetic foyaite and potassium rock got darker as the temperature increased.

In order to avoid the altering of the color perception of the parts, ideally, the color difference between coatings submitted to different illuminants must not exceed 5 units of CIElab (in the individual analysis of each parameter - L *, a * and b *) [16] and, from the data, it can be observed that the largest

difference occurred in the samples of potassic rocks, but this difference did not exceed 5 units, meaning that the difference of the samples does not change the perception of their color.

4. CONCLUSIONS

The substitutions of classical (and usually more expensive) raw materials in these types of studies are workable and expand the knowledge about the fluxes.

After analyzing the characteristics of the raw materials used and the experimental tests, it can be highlighted that the insertion of foyaite in the glaze formulation as a substitute source to the imported nepheline showed remarkably interesting results.

The best results were found when the rocks were used after the magnetic separation. In the in-natura matrix they presented a gray color which could not compete directly in the market with the separated foyaite.

The use of these rocks becomes quite interesting to reduce the use of imported raw materials and to strengthen or even create new opportunities for the ceramic industry, especially for Poços de Caldas (MG) where there are significant quantities of these raw materials.

The insertion of the separated and non-separated potassium rock in the glaze formulation, on the other hand, was not efficient due to its high iron contents still present in the matrix even after the magnetic separation.

Thus, alternative routes of treatment for these ores are necessary to achieve a decrease of the iron content more effectively.

The studies on these raw materials continue, aiming at their use as a flux in porcelainized stoneware tile compositions.

5. ACKNOWLEDGMENTS

The authors thank: Curimbaba Mining for supplying samples and analyzes.; Endeka Ceramics Ltda., for all the support and aid in this work; Daniela Gomes Horta, for assisting with the preparation of the samples; and Maurício Bergerman for the availability and attention, welcoming the project with the support of the Polytechnic School of the University of São Paulo.

6. REFERENCES

[1] ABC- Associação Brasileira de Cerâmica, https://abceram.org.br/materias-primas-naturais/. Acessado em 26/02/2020

[2] ASSIS, W.F., BERG, E.A.T., STEFANI R. "Desenvolvimento de Esmaltes com Formulações a Base de Riolito". *Cerâmica Industrial*, v. 7, n. 2, pp. 42-45, Março/Abril 2002.

[3] BRASIL. Departamento Nacional de Produção Mineral. Feldspato Sumário Mineral Brasileiro 2014. Brasília: DNPM, 2014.

[4] DEER, W.A. & HOWIE, R.A., ZUSSMAN, Y. *Minerais Constituintes das Rochas: Uma Introdução*. Editora Fundação Calouste Gulbenkian, Lisboa, Portugal, 3ª Edição, pp. 489-500,1966.

[5] EPPLER, R.A. "Selecionando Matérias-Primas para Esmaltes". *Cerâmica Industrial*, v. 7, n. 6, , pp. 14-18, Novembro/Dezembro 2002.

[6] HEVIA, R., CENTRITTO, N., OLIVEIRA, P.A.N., *et al. Introducción a los esmaltes cerâmicos.* CYTED, p. 224, 2002.

[7] LÓPEZ, E., CASTELLÓ, J.B.C., CORCONCILLO, E.C.; *Esmaltes y pigmentos cerâmicos.* Faenza Editrice Iberica, p. 330, 2001

[8] LUZ, A.B., LINS, A.F., *Rochas & Minerais Industriais.* Rio de Janeiro: CETEM/MCT, p. 867, 2005.

[9] MEDEIROS, P.N., TAVARES, M.T.S., AVELINO, K.A.R., *et al.* "Colagem de Barbotina e Esmaltação Cerâmica" In: *V Congresso Norte-Nordeste de Pesquisa e Inovação*, 2010, Maceió/AL. V Congresso Norte-Nordeste de Pesquisa e Inovação, p. 6, 2010.

[10] NANDI, V.S.; *Produção de frita para engobe a partir de resíduos sólidos gerados em estação de tratamento de efluentes de fabricação de revestimentos cerâmicos*. Dissertação (Mestrado em Ciência e Engenharia de Materiais) - Centro Tecnológico, Departamento de Engenharia Mecânica. Universidade de Santa Catarina, Florianopólis, p. 127, 2013.

[11] ROVERI, C.D., GODOY, L.H., ZANARDO, A., *et al.* "Caracterização tecnológica para aproveitamento de matéria-prima sienítica com nefelina". *Revista do Instituto Geológico*, São Paulo, pp. 27-39, 2013.

[12] SÁNCHES, E. "Matérias Primas para a Fabricação de fritas e Esmaltes Cerâmicos". *Cerâmica Industrial*. Maio/Agosto, pp. 32-40, 1997.

[13] SANTOS, N.C.C. "Análise econômica do uso de rochas potássicas da região de Poços de Caldas – MG como substitutos ao feldspato potássico minerado no nordeste do país". *XXVI Encontro Nacional de Tratamento de Minérios e Metalurgia Extrativa* - Poços de Caldas-MG, 2015. In: Anais do XXVI ENTMME, pp. 178-186, 2015.
[14] ULBRICH, H.H.G.J., *A Petrografia, a Estrutura e o Quimismo de Nefelina Sienitos do Maciço Alcalino de Poços de Caldas, MG-SP*. Tese de Livre Docência. Instituto de Geociências da Universidade de São Paulo, p. 360, 1984.
[15] DONDI, M. "Nepheline Syenites and other foid-bearing rocks" In: *Feldspar and other Fluxes for Ceramic Tiles* – Sources, processing, composition and technological behavior, Raw materials profile – chapter 10, pp. 151-172. CRAM EIP-RMs Commitment.
[16] SANTOS, S.F., ANDRADE, M.C., FRANCA, S.C.A., *et al.* "Estudo colorimétrico de fritas feldspáticas". *Cerâmica* [online], v.56, n.337, 2010.
[17] SULTANA, M.S., AHMED, A.N., ZAMAN, N.M., *et al.* "Utilization of hard rock dust in ceramic glaze formulation" IOP Conf. Series: *Materials Science and Engineering*. doi:10.1088/1757-899X/438/1/012018. 438 (2018) 01. 2018
[18] BRAGANÇA, S., LENGLER, H.C.M., BERGMANN, C.P. "Rocha com espodumênio como fundente para massas cerâmicas tradicionais**"** *Cerâmica* v. 56, pp. 291-299, 2010.

ORCID

José Tadeu Gouvêa Junior https://orcid.org/0000-0002-8464-916X
Sylma Carvalho Maestrelli https://orcid.org/0000-0002-5037-4276
Luciano Luis da Silva https://orcid.org/0000-0002-5806-7596
Carolina Del Roveri https://orcid.org/0000-0002-7721-9014